

CLAIMS

1. Method for removal of metal cations contained in a liquid in which said liquid is brought into contact at a temperature higher than or equal to 60°C, with a chelating ion exchange resin formed from polyazacycloalkane grafted on a solid support, said resin having been conditioned, previously to said contacting, at a pH of 4 to 6.
2. Method according to Claim 1 in which the contacting is carried out at a temperature of 60 to 80°C.
3. Method according to Claim 1 in which the conditioning pH is 4 to 5.
4. Method according to any one of Claims 1 to 3 in which the conditioning of said resin is carried out by contacting said resin with a buffer solution, especially aqueous, in which the pH is 4 to 6, possibly preceded and/or followed by a rinsing of the resin with a major solvent of the liquid to be treated, especially with distilled water.
5. Method according to Claim 1 carried out continuously, said resin being placed in at least one column passed through by a current of liquid to be treated.

6. Method according to Claim 1 comprising, in addition, a regeneration step of said resin, when the latter is saturated by the fixed metals.

5           7. Method according to Claim 5 and Claim 6 in which said regeneration is carried out by passing a regeneration solution through the column(s) in the reverse direction from the direction of circulation of the liquid to be treated.

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8. Method according to Claim 7 in which said regeneration solution is chosen from the acid solutions, for example, nitric acid.

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9. Method according to Claim 7 or Claim 8 in which at the end of the regeneration step, said regeneration solution containing the metals initially fixed on the resin is treated to recover the metals.

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10. Method according to any one of Claims 1 to 9 comprising a prior step for treatment of the liquid by contacting with an ion exchanger or organic or mineral adsorbent different from said polyazacycloalkane resin grafted on a support.

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11. Method according to Claim 10 in which said adsorbent is chosen from the silica gels.

12. Method according to Claim 10 in which said ion exchanger is chosen from resins of the polyacrylate type, resins of the AMBERLITE® type.

5 13. Method according to Claim 10 in which said prior treatment step is carried out continuously, said ion exchanger or adsorbent being placed in at least one column passed through by a current of liquid to be treated and positioned upstream of said column filled  
10 with resin.

14. Method according to Claim 11 in which said ion exchanger or adsorbent is regenerated when it is saturated by the fixed metals under the same conditions  
15 as the resin and at the same time as regeneration of the latter and with the same regeneration solution.

15. Method according to Claim 1 in which said metal cations to be removed are metal cations chosen from  
20 transition metals, heavy metals, metals from group IIIA of the periodic table, lanthanides, actinides and alkaline-earth metals.

16. Method according to Claim 13 in which said  
25 metal cations are chosen among the cations of U, Pu, Am, Ce, Eu, Al, Gd, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, B, Au, Hg, Pb, As, Ca, Sr, Mg, Be, Ba and Ra.

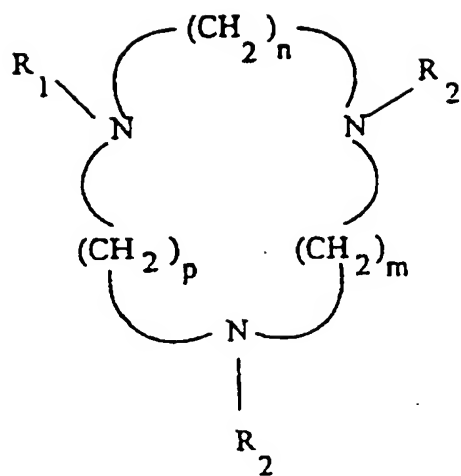
17. Method according to any one of Claims 1 to 16  
in which the treated liquid is an aqueous liquid.

18. Method according to any one of Claims 1 to 17  
5 in which the treated liquid is a radioactive aqueous  
effluent with low activity.

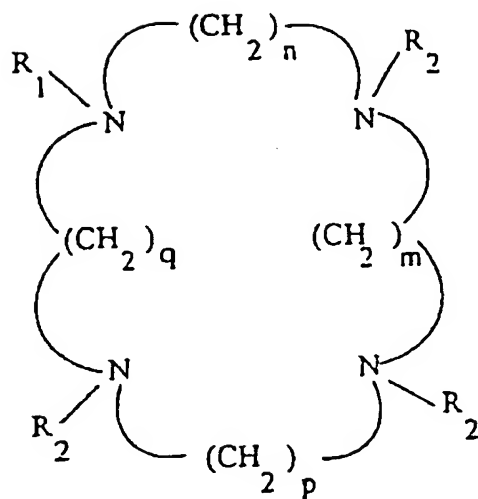
19. Method according to Claim 19 in which said  
effluent is the aqueous effluent with low activity  
10 originating from the industrial evaporator of the  
treatment installation of effluents from a nuclear  
installation.

20. Method according to Claim 16 and Claim 17 in  
15 which the liquid is a biological fluid, such as blood and  
the cations removed are copper and aluminium.

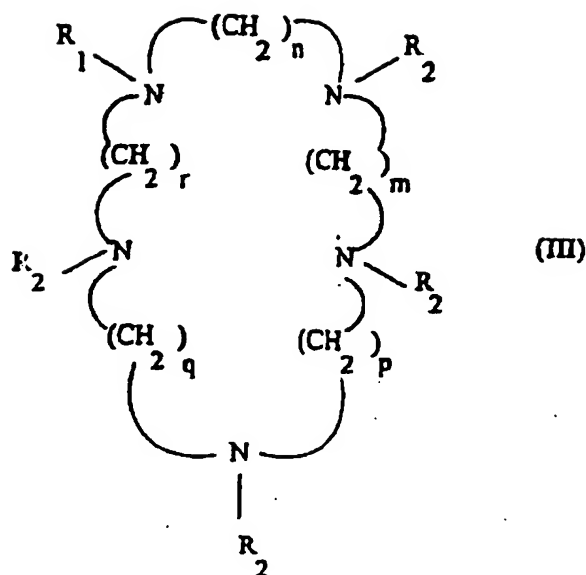
21. Method according to any one of Claims 1 to 20  
in which said chelating ion exchange resin formed from  
20 polyazacycloalkane grafted on a solid support fulfils one  
of the three formulas (I), (II) and (III) below:



(I)



(II)



in which  $n$ ,  $m$ ,  $p$ ,  $q$ ,  $r$  which may be the same or different are equal to 2 or 3,  $R_1$  is a solid support,  $R_2$  represents the hydrogen atom or the  $(CH_2)_2-R_3$  group,  $R_3$  being a functional group chosen from the group formed by  $COOH$ ,  $CONH_2$ ,  $CH_2OH$ ,  $CN$  or  $COOR_4$ ,  $R_4$  representing an alkyl or benzyl group, or  $R_2$  represents the  $-(CH_2)-R_5$  group,  $R_5$  representing  $COOH$  or  $PO_3R_6$ ,  $R_6$  representing an alkyl group or hydrogen.

22. Method according to any one of Claims 1 to 21 in which the solid support is an organic polymer that may or may not be crosslinked.

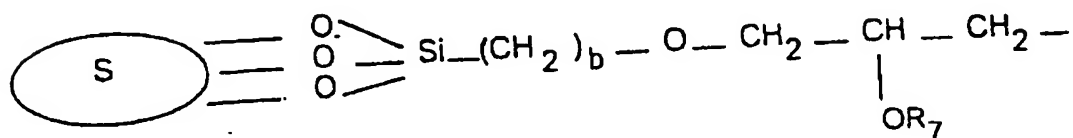
23. Method according to Claim 22 in which the solid support is a residue of an organic polymer that may or

may not be crosslinked with alkyl halide end, preferably alkyl chloride end.

24. Method according to Claim 23 in which the solid support is a residue of chloromethyl polystyrene.

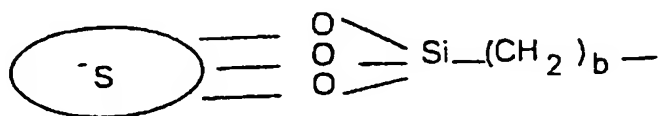
25. Method according to Claim 24 in which the grain size distribution of said chloromethyl polystyrene is between 20 and 400 mesh and, preferably, between 20 and 70 mesh.

26. Method according to Claim 21 in which R1 is a solid support derived from silica fulfilling formula:



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where [sic; or] the formula:

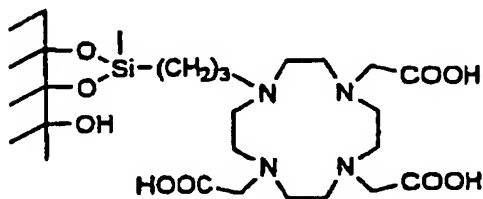


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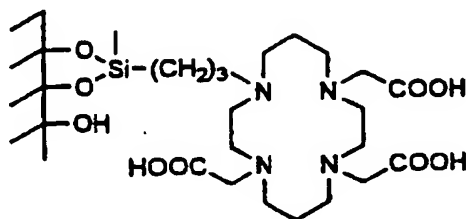
S representing a silica gel, b being between 1 and 4 and preferably equal to 3 and R7 being an alkyl group or a hydrogen atom.

5        27. Method according to Claim 26 in which the grains size distribution of the solid support derived from silica is between 20 and 400 mesh and, preferably between 20 and 70 mesh.

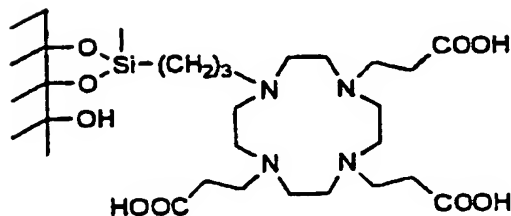
10       28. Method according to Claim 21 in which said resin is chosen from the following resins:



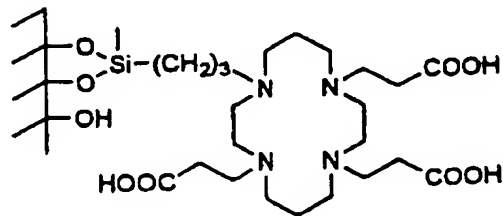
**Si2222trA**



**Si2323trA**



**Si2222trPr**



**Si2323trPr**



29. Method according to Claim 1 in which said solid support is silica, and said resin is prepared by a method in which silica is reacted with a spacer arm, then with azacycloalkane and then the substitution of the free  
5 amine functions of the polyazacycloalkane is carried out by groups especially including a carboxylic function.

30. Method according to Claim 1 in which said solid support is silica and said resin is prepared by a method  
10 in which first, an unsubstituted polyazacycloalkane, such as cyclam or cyclene is reacted with a spacer arm, then said polyazacycloalkane carrying a spacer arm is grafted on the silica.

31. Method according to Claim 30 in which in  
15 addition, said polyazacycloalkane carrying a spacer arm is functionalized prior to its grafting on the silica.

32. Method according to Claim 30 or Claim 31 in  
20 which the amount of polyazacycloalkane grafted per unit weight of solid support, such as silica is greater than 0.4 mmol.g<sup>-1</sup>.

33. Installation for removal of metal cations  
25 contained in a liquid comprising at least a column filled with a chelating ion exchange resin formed from a polyazacycloalkane fixed on a support, means for causing a current of liquid to be treated to pass through said column, means for conditioning said resin at a pH of 4 to

6 and means for heating said resin to a temperature greater than or equal to 60°C.

34. Installation according to Claim 33 comprising,  
5 in addition, a column filled with ion exchanger or organic or mineral adsorbent different from said polyazacycloalkane resin grafted on a support, placed upstream of said column filled with resin.

10 35. Installation according to Claim 33 or Claim 34 comprising in addition, means for regenerating said chelating ion exchange resin and possibly, said ion exchanger or organic or mineral adsorbent.